

Jet-Cooked Starch–Oil Composite in Polyurethane Foams

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ABSTRACT: A new jet-cooked starch–oil composite has been blended with a polyester polyol and then reacted with isocyanate to give a polyurethane foam. Infrared spectroscopy and microscopy have been used to examine the resultant products. Infrared spectra have shown the products contain the urethane structures and light and electron microscopy have shown the differences in the cell wall structures and networks of the foams when compared to the control foams. Inclusion of the starch–oil composite in the formulation resulted in increased viscosity of the reaction mixture as well as a more irregular cellular structure and a rougher texture of the cured foam. Larger cells were more abundant and there was more evidence of tearing during expansion. The scanning electron photomicrographs show the open-cell structure of both the control and blended foams and their reticular network, which is more uniform in the control. This examination provides insight into the foaming process and provides information to make the necessary adjustments for acquiring the desired polymeric product. Incorporation of the starch–oil composite in polyurethane foams provides a new dimension of possibilities for enhancing their physical, functional, and environmental properties. © 1997 John Wiley & Sons, Inc. * J Appl Polym Sci **64**: 1355–1361, 1997

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INTRODUCTION

Polymer blends emerged in the late 1970s, and these polymeric materials have shown substantial growth since the 1980s.¹ New polymers are rarely introduced, but many new products are made possible by the development of new starting materials. The blending process has been cost effective for enhancing properties and developing products with desired performance. In the search for new and promising blends, various analytical methods are used to determine the products generated from the reactions. With polyurethane (PU) foams, the reaction of polyols with isocyanates in the presence of water and catalysts is quite com-

plex.² Infrared spectroscopy has been used to analyze the chemical composition of such foams.³ In this investigation, we have incorporated different levels of Fantesk, an extremely stable jet-cooked composite of oil, water, and starch,^{4–7} a natural polyol into PU foam formulations. Fantesk is a starch–oil composite prepared by a jet cooking that uses the high temperature and turbulence within the cooker to uniformly disperse the oil component within the starch–water matrix as small droplets. These droplets will not separate or coalesce, even after prolonged standing and after the product is dried.

Co-jet cooking of starch with nonstarch materials is a new area of research that has been virtually unexplored. Incorporation of this composite in PU foams provides a powerful approach for the enhancement of foam properties, the addition of oil-soluble components, and the introduction of biodegradability to foam products. With the use

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Table I Ingredients in Foam Formulations^a

Fantesk	Polyester Polyol	Isocyanate	Water
0	50	33	1.5
5	45	42	2.0
10	40	43	2.0
15	35	44	2.0
20	30	45	2.0

^a Ingredients are given in parts by weight. All formulations contained 0.05 parts dibutyltin dilaurate catalyst.

of Fourier transform infrared spectroscopy (FTIR) and microscopy, characterizations of these new foam formulations were compared to study the resultant conversion products. These techniques can be used as aids in selecting catalysts, modifying isocyanate indices, and/or evaluating the mixing technique.

EXPERIMENTAL

Materials

The materials used in the foam formulations were polyester polyol (Lexorez 1102-50A, Inolex Chemical Co., Philadelphia, PA), polymeric isocyanate (PAPI 27, Dow Chemical Co., LaPorte, TX), dibutyltin dilaurate (Aldrich Chemical Co., Milwaukee, WI), and Fantesk, a stable emulsion of soy oil, water, and cornstarch produced, and drum dried at the National Center for Agricultural Utilization Research in Peoria, IL.

Test Methods and Preparation of PU Foams

Dry solids of the composite were determined by drying at 105°C for 4 h in a mechanical convection oven (model STM 135, Precision Scientific, Chicago, IL).

Hydroxyl values were determined by Association of Official Analytical Chemists (AOAC) Methods 28.016-28.017 (American Oil Chemists' Society Method).⁸

Foams were prepared by adding polymeric isocyanate to a mixture of the polyol (including Fantesk), dibutyltin dilaurate, and water. Formulations and a description of raw materials are given, Tables I and II. Ingredients were added in sequence as listed above, with Fantesk additions of 10, 20, 30, and 40%. The quantities of Fantesk (dry basis) were based on percentages of the total

weight of the polyols. The quantity of isocyanate added in each formulation was dependent on available hydroxyl content. Four replicate foams were prepared with and without Fantesk additions. The ingredients were mixed for 30 s at 11 hertz, or to the creamy stage, in a blender (Model 5203 P1 with a 8051 Waring Blendor adapter, Eberbach Corp., Ann Arbor, MI) equipped with a Fincor 5200 adjustable frequency AC motor control (Eberbach Corp., Ann Arbor, MI). The mixtures were poured into 1-L containers and allowed to rise at room conditions.

Foams were removed from the containers after 1 h. Specimens for FTIR analysis and microscopy were removed with a hand saw from near the center of the foam.

Fourier Transform Infrared Spectrometric Analysis (FTIR)

Prior to FTIR analysis, all foam samples were dried under vacuum at 30°C for 24 h. Test specimens were ground, mixed with KBr, and pressed into transparent KBr disks. This was accomplished by pulverizing 5.0 mg of specimen for 3 min at liquid nitrogen temperature in a stainless steel vial containing two stainless steel ball bearings on a mixer mill (Brinkmann Instruments Inc., Subsidiary of Sybron Corp., Westbury, NY). After warming to ambient temperature, 95.0 mg of spectral grade KBr (Spectra-Tech Inc., Samford, CT) was added to the vial. All weighings and transfers of specimens were done in a dry box to prevent moisture absorption by the hygroscopic KBr. The specimen in KBr was then pulverized on the amalgamator (Wig-L-Bug, Crescent Dental Mfg. Co., Lyons, IL) for 60 s at liquid nitrogen temperature in the same vial. At ambient temperature, 25 mg of the pulverized KBr mixture was diluted to 750 mg in KBr and mixed without the stainless steel balls on the amalgamator. Finally, 300 mg of the pulverized KBr mixture was transferred in the dry box to a 13 mm KBr die (Perkin-Elmer Corp., Analytical Instruments, Norwalk, CT), and the die was evacuated for 5 min before pressing *in vacuo* at 110 MPa on a laboratory press (Fred S. Carver, Menomonee Falls, WI). Infrared spectra were measured on an FTIR spectrometer (Model RFX-75, KVB-Analect, Irvine, CA) equipped with a TGS detector. Interferograms were processed on an APT-824 array processor using triangular apodization for linear response. Spectra were acquired at 4 cm⁻¹ resolution and signal averaged over 32 scans with no

Table II Description of Materials

Name	Description
Lexorez 1102-50A	Crosslinked di(ethylene glycol) adipate
Fantesk	Jet-cooked composite of an emulsion of soy oil, water, and cornstarch
PAPI 27 Polymeric MDI	Diphenylmethane diisocyanate (containing methylene bisphenyl isocyanate) and polymethylene polyphenyl isocyanate
Dibutyltin dilaurate	Organotin compound

zero filling. The interferometer and specimen chambers were purged with dry nitrogen to remove spectral interference from water vapor and carbon dioxide.

Light Microscopy

Blocks of cured foam were cut into portions approximately $1 \times 1 \times 2$ cm. Thin sections of foam were cut by hand with a No. 11 stainless steel scalpel blade. Sections from 0.3 to 0.5 mm in thickness were selected because they contained enough material to prevent disintegration while allowing visualization of the cell structure. Sections were positioned on a pair of hairs stretched across the opening of a dark chamber and illuminated from above with a Schott fiber optic ring illuminator. Photographs were made through a Zeiss stereomicroscope.

Transmitted light micrographs were prepared by selecting flat portions of the walls of the largest cells, placing them on a microscope slide, and photographing them through a Zeiss photomicroscope system either uncovered (low magnification) or surrounded with immersion oil and covered with a coverslip (high magnification). For the low magnification images, bright-field illumination was used, but the condenser aperture was reduced to enhance specimen contrast. High-magnification images were obtained with phase contrast optics.

Scanning Electron Microscopy (SEM)

Specimens were mounted on aluminum stubs using double-sided carbon tape and were coated with gold-palladium (60 : 40) to a thickness of about 0.015 micron in a sputter coater. The coated specimens were observed in a SEM (Model JSM-6400, JEOL Inc., Peabody, MA) at a specimen angle of 0° . Accelerating voltage was 10 kV, and final aperture was 200 microns.

RESULTS AND DISCUSSION

General

The starch-oil composite had a hydroxyl value of 117 vs. 50 for the polyester. The higher value permitted more crosslinking but both values were in the range of polyols used for preparing flexible foams.⁹

FTIR Analysis

Spectra of FTIR data are one way to determine the conversion of isocyanate as a parameter in PU foams. Spectra are shown for the initial ingredients (Fig. 1) and after their incorporation into PU foams (Fig. 2). The phenyl peak was used as the reference point for comparison because its absorp-

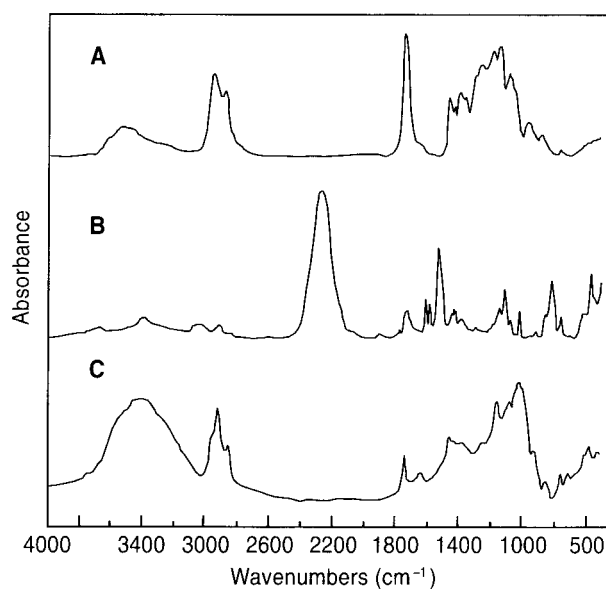


Figure 1 Fourier transform infrared spectrometric analysis of (A) polyester polyol (B) PAPI 27 isocyanate and (C) Fantesk (starch-oil composite).

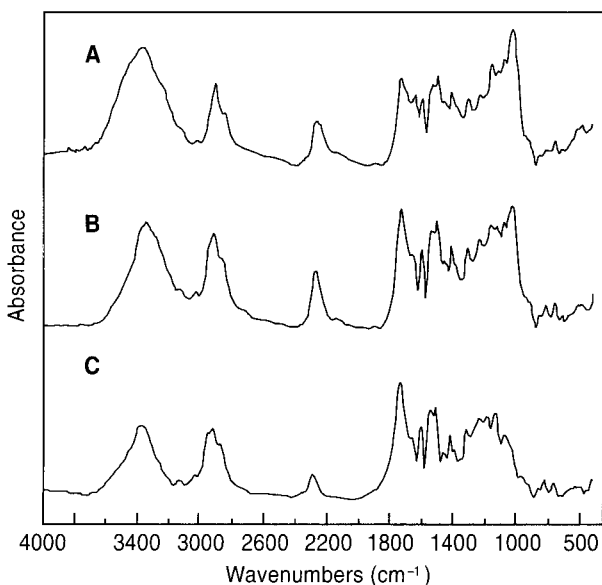


Figure 2 Fourier transform infrared spectrometric analysis of foams (A) 40% of polyol as Fantesk (B) 20% of polyol as Fantesk and (C) control containing only polyester polyol.

tion remained constant for a given polyol/isocyanate formulation and was independent of the reaction between the two.² The majority of the isocyanate used in a given formulation was distributed in the usual species of reaction products (urethane, urea, biuret, allophanate, isocyanurate, etc.) with some unreacted isocyanate end groups appearing at 2277 cm^{-1} . Because of the equal quantities of water in the experiments, a large excess of isocyanate was used in each formulation and the isocyanate/phenyl ratio ($2277/1600\text{ cm}^{-1}$) remained essentially constant with increasing Fantesk addition in the formulations.

FTIR spectra of reaction products showed evidence of polyurethane structure. Secondary amine bands of the urethane appeared at $3310\text{--}3350\text{ cm}^{-1}$. The urethane carbonyl itself absorbs at 1730 cm^{-1} ; however, this band was obscured by the much stronger carbonyl band from the ester moiety in the polyester polyol. Nevertheless, the presence of polyurethane was suggested by the appearance of C—O stretching (1320 cm^{-1}) in the spectrum of the control [Fig. 2(C)]. Also, indirect evidence of urethane formation appeared in all product spectra (Fig. 2) as the N—H bending band at 1660 cm^{-1} , which arose from the allophanate formed in the reaction of isocyanate with nascent and existing urethane. Indeed, the change in urethane content could be followed by monitoring the allophanate NH/phenyl ratio ($1660/1600$

cm^{-1}), which steadily increased with increasing Fantesk content. Evidence of other usual products of polyisocyanate reactions were the isocyanurate bands at 1414 cm^{-1} and the small carbodiimide bands at 2135 cm^{-1} shown in Figure 2. The increased starch content in the formulations were clearly indicated by the increased carboxyl (3350 cm^{-1}) and C—O (1020 cm^{-1}) bands in the Fantesk product spectra [Fig. 2(A) and (B)] over the control spectrum.

The fact that the unreacted isocyanate/phenyl ratio did not change significantly as the starch/polyester ratio increased indicates that the starch reacted with the isocyanate to form urethane crosslinks with the starch as well as the polyester polyol. This would result in a highly branched and interconnected molecular structure with unique physical properties. This crosslinking would contribute to the rigidity of the Fantesk foams.

Light Microscopy

The control foam consisted of a network of material forming more or less spherical cells of a wide range of sizes up to about 1 mm in diameter [Fig. 3(A)]. Discontinuities in the cell walls suggested tearing of the network during expansion to yield an open cell structure. Foams became more rigid with additional Fantesk. This could be related to the viscosity of the reaction mix and the tearing of the network during expansion. Transmitted light microscopy of the control foam revealed a smooth, uniform, transparent solid phase throughout the network [Fig. 3(B)]. The foam containing 20% Fantesk [Fig. 3(C)] also showed a cellular structure, although the cells were more irregular in shape than the control foam and the walls had a rougher texture. There was more evidence of tearing during expansion, and large cells were more abundant compared with the control foam [Fig. 3(C)]. The cell wall material [Fig. 3(D)] was rougher in texture than the control foam and contained abundant smaller cells and bubbles. The 40% Fantesk foam [Fig. 3(E)] had a very uneven texture with irregular cells and much evidence of tearing during expansion. The appearance of the solid phase was somewhat more clumped and matted than the 20% Fantesk foam. Fantesk (starch) may increase the adhesive quality of the solid phase; this would be consistent with the clumped or matted appearance of the network. These qualities were proportional to the amount of Fantesk added. Transmitted light microscopy of the cell walls of the 40% Fantesk foam

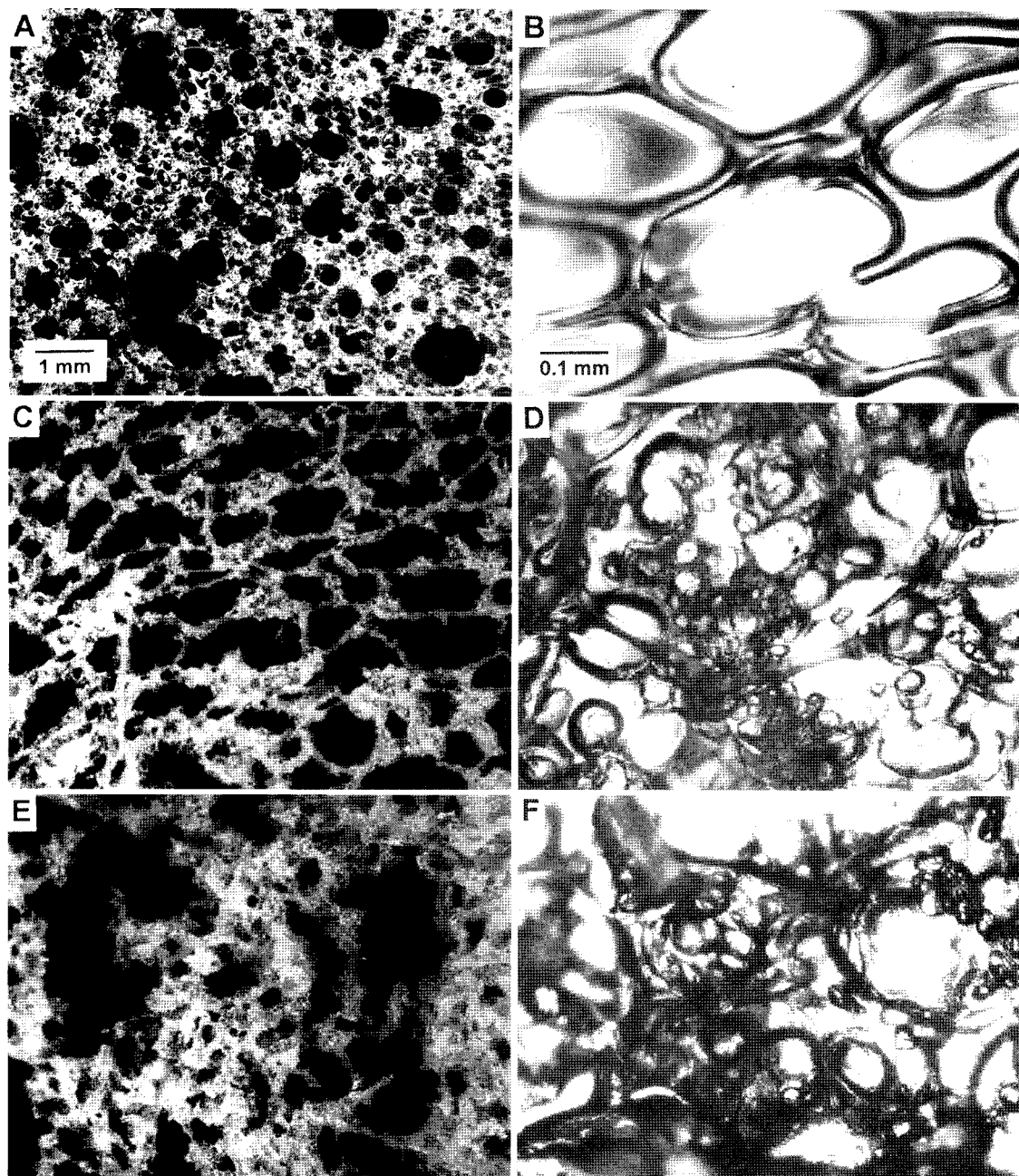


Figure 3 Light micrographs of foams (A, B) control polyester (C, D) 20% of polyol as Fantesk, and (E, F) 40% of polyol as Fantesk (A, C, and E) thin slices of foam photographed with incident (reflected) light, all at the same magnification. (B, D, and F) transmitted light micrographs of single-cell wall pieces, all at the same magnification.

revealed the same abundance of small cells and bubbles, but the texture of the solid phase was rougher than the 20% Fantesk foam [Fig. 3(F)].

Examination of pieces of cell wall from the 40% Fantesk foam with a $100\times$, oil immersion phase contrast objective revealed two distinctly different

domains in the solid phase. One type of structure appeared in discrete granules and consisted of a heterogeneous background with spherical inclusions [Fig. 4(A), left, and Fig. 4(B)]. The size distribution of the spherical inclusions was consistent with that of the oil droplets in the Fantesk

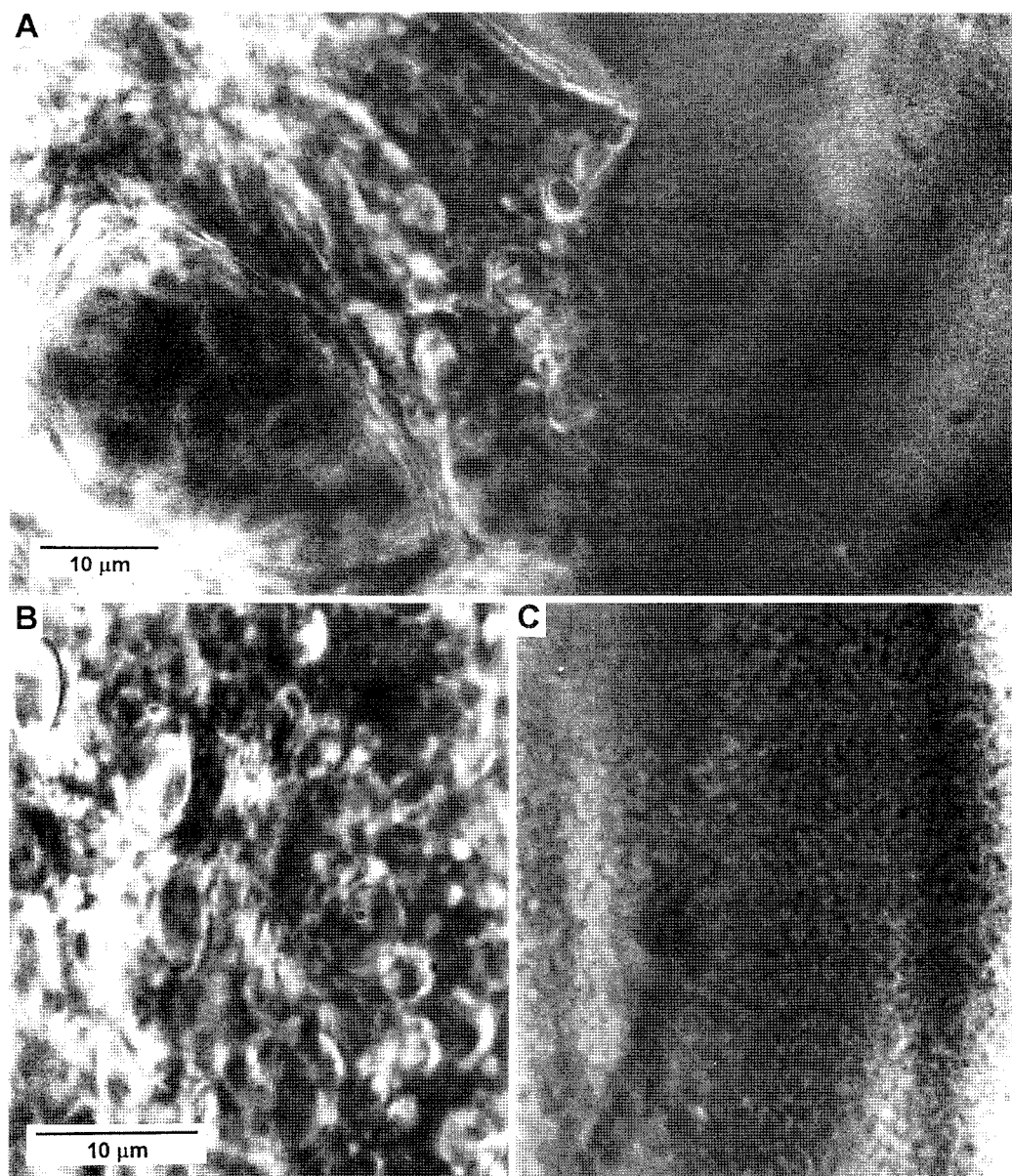


Figure 4 Phase contrast micrographs of pieces of cell wall from a foam with 40% of polyol as Fantesk. (A) sharp discontinuity between a heterogeneous granule (left) and the more uniform background (right). (B) higher magnification of the granule domain, interpreted as consisting of the Fantesk composite. (C) higher magnification (same as B) of the background domain, showing uniform mottling or granularity.

composite.⁶ Outside of these granules, which were interpreted to represent the milled, drum-dried Fantesk powder dispersed in the polyester resin, the solid phase consisted of a relatively uniform material with a distinctly granular or mottled appearance [Fig. 4(A), right, and Fig. 4(C)]. The solid phase of the control foam was devoid of any discernible structure either with bright or phase contrast microscopy (not shown).

Foams prepared with added soy oil or with added starch only (data not shown) also possessed a granular, mottled solid phase in contrast to the transparent, structureless solid phase of the control polyester foam. This strongly suggests that in addition to the inclusion of the native, undissolved Fantesk composite particles suspended in the reaction mixtures, either soy oil or starch, or both, dissolved into the polyester phase and affected

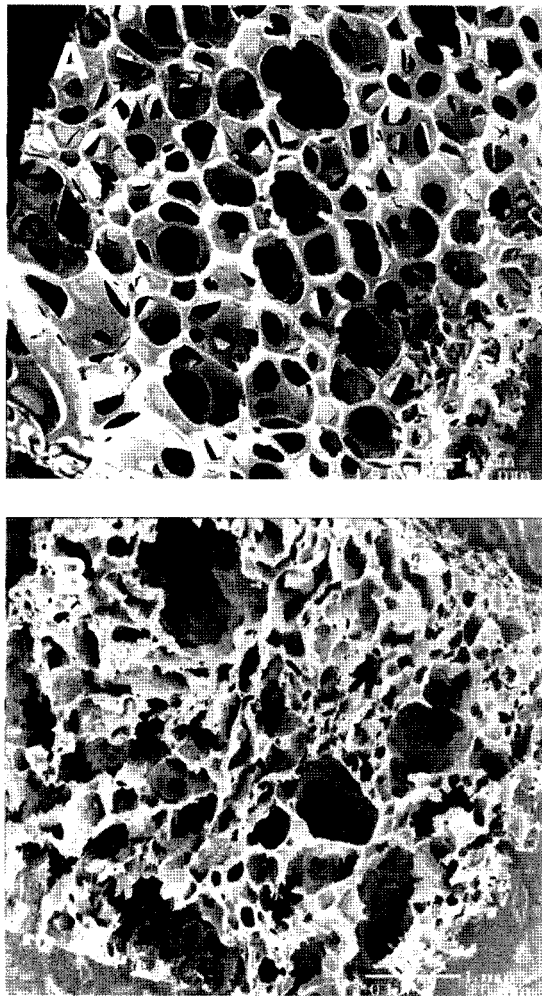


Figure 5 Scanning electron micrographs of foams (A) control and (B) 40% of polyol as Fantesk.

the background structure of the resulting reaction product in some way.

The oil component of the Fantesk could be exploited to carry into the foam any oil-miscible additive. The starch component, in addition to changing the rigidity and cell structure of the foam, could introduce biodegradability to the extent that the starch was accessible to water and microbes.

SEM

Photomicrographs of the control foam [Fig. 5(A)] and the 40% Fantesk foam [Fig. 5(B)] show evidence of the open-cell structure. Observing the surfaces permits studying the reticular cellular network, which is more uniform in the control foam.

CONCLUSIONS

FTIR spectroscopy and microscopy revealed the nature of products from reactions of isocyanate with a jet-cooked starch-oil composite and polyester polyol blend to produce a modified polyurethane structure. The usual products of isocyanate reacting with a polyol were indicated. However, microscopy showed changes brought about by the addition of the composite as a polyol on the cell walls of the foam as well as the reticular network. The cell walls containing the blended polyols were thicker with a more complex texture. These results show that it is possible to produce polyurethane foams with altered physical, functional, and environmental properties by further manipulation of the amount and type of starch-oil composite additive.

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REFERENCES

1. M. Z. Yue and K. S. Chian, *J. Appl. Polym. Sci.*, **60**, 597 (1996).
2. D. Bhattacharjee and R. Engineer, *Proceedings of the Polyurethanes 1994 Conference*, 1994, p. 280.
3. R. D. Priester, Jr., J. V. McClusky, R. E. O'Neill, R. B. Turner, M. A. Harthcock, and B. L. Davis, *Proceedings of the SPI 33rd Annual Polyurethane Technical Marketing Conference*, 1990, p. 527.
4. K. Eskins and G. F. Fanta, U.S. Pat. Appl. 08 233,173, Filed April 26, 1994.
5. G. F. Fanta and K. Eskins, *Carbohydr. Polym.*, **28**, 171 (1995).
6. K. Eskins, G. F. Fanta, F. C. Felker, and F. L. Baker, *Carbohydr. Polym.*, **29**, 233 (1996).
7. C. A. Knutson, K. Eskins, and G. F. Fanta, *Cereal Chem.*, **73**, 185 (1996).
8. AOAC *Official Methods of Analysis*, 13th ed., Association of Official Analytical Chemists, Washington, DC, 1980.
9. G. Woods, *The ICI Polyurethanes Book*, 2nd ed., ICI Polyurethanes and Wiley, Chichester, UK, 1990, p. 35.